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A plasmonic "ac Wheatstone bridge" circuit for high-sensitivity phase measurement and single-molecule detection

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In this paper, a plasmonic "ac Wheatstone bridge" circuit is proposed and theoretically modeled for the first time. The bridge circuit consists of three metallic nanoparticles, shaped as rectangular prisms, with two nanoparticles acting as parallel arms of a resonant circuit and the third bridging nanoparticle acting as an optical antenna providing an output signal. Polarized light excites localized surface plasmon resonances in the two arms of the circuit, which generate an optical signal dependent on the phase-sensitive excitations of surface plasmons in the antenna. The circuit is analyzed using a plasmonic coupling theory and numerical simulations. The analyses show that the plasmonic circuit is sensitive to phase shifts between the arms of the bridge and has the potential to detect the presence of single molecules. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3195071]

I. INTRODUCTION

Localized surface plasmon resonances (SPRs) in metallic nanoparticles arise from the interaction between the conduction electrons in the metal and the electromagnetic fields associated with the electron charges and their motions. The electric fields extend into the region about the nanoparticle, so that the frequency of the plasmon resonance depends on the local electric permittivity. This effect has generated substantial interest in the application of metallic nanoparticles for sensing molecules.[1–3] The presence of molecules on or near the surface of the nanoparticle perturbs the local permittivity, which alters the SPR. The change in the resonance frequency is detected by a shift in the spectrum of light scattered from the nanoparticle. Englebienne[4] observed these shifts when ensembles of colloidal gold nanoparticles coated with antibodies were brought into contact with their respective antigens, providing stimulus for the development of low cost, high throughput sensors for chemical screening. In clusters of metal nanoparticles, it has been observed that changes in the local permittivity create SPR shifts of up to 1 nm for refractive index changes of 0.005.[5,6] Spectral studies of individual silver nanoparticles showed similar sensitivities[7] and allowed the observation of the adsorption of large molecules onto the nanoparticles.[8] The effect was used to demonstrate biomolecular recognition by observing the wavelength shift of resonances in individual gold nanospheres with the binding of proteins.[9] While the method is very sensitive, it relies on resolving the spectral shifts and it is limited by the natural width of the resonance, the strength of the scattering, and the resolution of the spectrometer. Despite the usefulness of these simple systems for sensing, there has been little work on the rational design of nanoparticle systems for this purpose.

As an alternative, we can treat the nanoparticle as a plasmonic device and view the resonances as due to the coupling of the nanoparticle inductance and the capacitance.[10–13] In this circuit model, the change in the local permittivity produces a change in the capacitance, which is responsible for the shift in the resonant frequency of the plasmonic circuit. There are many circuit designs for measuring changes in the values of electrical components: Probably the most well known is the ac Wheatstone bridge. This circuit consists of two "arms" that are balanced so that the voltages between two points of the arms have the same amplitude and are in phase. A small phase shift in one of the arms, as would arise due to a change in capacitance, unbalances the circuit creating a large voltage output. We propose for the first time a plasmonic version of the ac Wheatstone bridge circuit that uses phase-sensitive coupling of localized surface plasmons in nanoparticles to produce an optical signal when the bridge becomes unbalanced. We investigate the sensitivity of the plasmonic circuit to phase shifts and discuss its application to sensing individual molecules.

The circuit is designed by treating each nanoparticle as a plasmonic circuit component and arranging them to form the plasmonic Wheatstone bridge as shown in Fig. 1(a). The equivalent circuits are given Figs. 1(b) and 1(c). The main elements of the circuit are two parallel nanoparticles, represented here as rectangular prisms or stripes, that form the two arms of the bridge. One of these nanoparticles acts as a reference arm while the other is used to sense changes in the local environment. Localized SPRs are excited in these nanoparticles by light polarized parallel to their long axes. When both nanoparticles are resonant at the same frequency, the surface plasmons oscillate in phase so that the electric charges that accumulate at their ends have the same sign and are in phase. Under this condition they are unable to excite a SPR in a third nanoparticle bridging the two arms of the circuit. This nanoparticle detects the imbalance of the circuit and acts as an optical antenna to outcouple the surface plasmon signal. When there is a shift in the resonant frequency of the sense nanoparticle, the surface plasmons no longer

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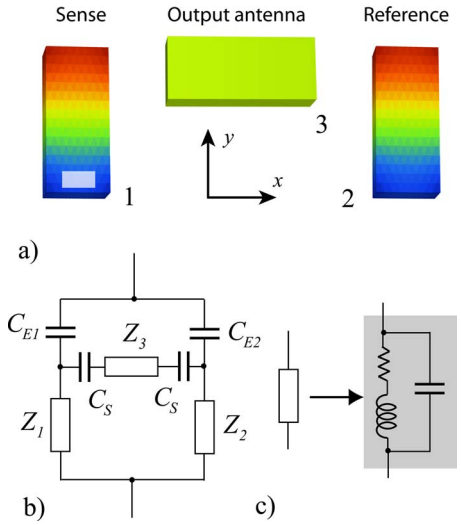

FIG. 1. (Color online) An example of a plasmonic ac Wheatstone bridge circuit. (a) A circuit consisting of three metal nanoparticles in the form of rectangular prisms or stripes. The colors represent the surface dipole distribution associated with the fundamental eigenmode excited by light polarized in the y direction (blue positive and red negative). The gray patch on the sense nanoparticle 1 is the sample region where the binding of molecules unbalances the circuit. (b) The equivalent circuit: C_E represents the coupling of the circuit to the electric field of the applied light; C_S are the capacitive couplings between the output nanoparticle 3 and the two nanoparticles at either end and Z is the impedance of the nanoparticles. (c) The impedance of each nanoparticle can be modeled by a resonant inductor-capacitor (LC) circuit with resistive losses.

oscillate in phase. This means that, at any moment in time, the electric charges at the ends are different and therefore different charges are induced across the bridging nanoparticle, exciting a surface plasmon. This surface plasmon then radiates light polarized perpendicular to the incident light.

In our analysis below we will show that the light radiated from the bridging antenna nanoparticle has an amplitude proportional to the phase difference between the SPRs in the arms of the circuit. While plasmonic three-stripe configurations have been investigated previously, to demonstrate electromagnetically induced transparency[14] and Fano resonances,[15] their phase sensing property and ability to act as sensors for molecules have not been reported. More generally, other nanoparticle shapes could be used for the plasmonic circuit but we focus on rectangular prisms as they are relatively easy to manufacture using electron-beam lithography.

II. ANALYSIS OF THE PLASMONIC BRIDGE CIRCUIT

The plasmonic bridge circuit can be analyzed by considering the individual plasmonic resonances of the three nanoparticle components and then using a plasmonic coupling theory[16] to describe the interactions between them. The coupling theory is based on an "electrostatic" approximation,[17,18] which is a simplification of the boundary element method.[19,20] Within this approximation, the nanoparticles are assumed to be much smaller than the wavelength of the incident radiation so that the system appears to be in a spatially uniform electric field that oscillates at the frequency of the incident light. The electric field excites one or more SPRs that can be described by a set of eigenfunctions. Specifically, nanoparticle j has a set of dipole resonances $\mathbf{p}_j^k$ associated with eigenmodes k. The scattering of the incident light depends on the strength of the dipole moment $\mathbf{P}_j$, which is given by a sum over the excited modes

$$\mathbf{P}_j = \sum_k a_j^k(\omega)\mathbf{p}_j^k, \tag{1}$$

where the amplitude $a_j^k(\omega)$ of the kth resonance is given by

$$a_j^k(\omega) = \frac{2\gamma_j^k \varepsilon_b(\varepsilon(\omega)-\varepsilon_b)\eta_j \mathbf{p}_j^k \mathbf{E}_0}{\varepsilon_b(\gamma_j^k+1)+\varepsilon(\omega)(\gamma_j^k-1)}. \tag{2}$$

The parameter γ_j^k is the eigenvalue associated with the kth eigenmode, $\mathbf{E}_0$ is the vector amplitude of the incident electric field, and η_j is a constant. Implicit in this formula is a time dependence of the incident field of $\exp(-i\omega t)$. A resonance occurs when the real part of the denominator is zero, which, given the electric permittivity $\varepsilon(\omega)$ of the nanostructure and the permittivity of the background medium ε_b, determines the resonant frequency ω_R. Equation (2) is applicable to any metallic nanoparticle. For example, the fundamental mode of a sphere is given by $k=1$, $\gamma_j^1=3$ and the zero in the denominator then yields the condition for a Fröhlich resonance.[21]

For our analysis, it is useful to express the amplitude $a_j^k(\omega)$ in terms of the phase shift ϕ of the oscillations as they move off resonance, which can occur if a molecule bonds to the nanoparticle thereby changing the local permittivity. Close to resonance, the amplitude in Eq. (2) has a form $a_j^k \propto (R+i\Gamma)^{-1}$ where $R=0$ at resonance and the damping is determined by Γ, which is approximately constant with frequency. Defining the phase shift by $\tan\phi = R/\Gamma$, the amplitude can be expressed as

$$a_j^k(\omega) = a_j^k(\omega_R)\cos\phi\exp(i\phi), \tag{3}$$

where $a_j^k(\omega_R)$ is the amplitude at resonance. The scattering cross section for dipole radiation is

$$C_{\text{sca}} = \frac{{k_0}^4}{6\pi}\left|\frac{\mathbf{P}}{E_0}\right|^2, \tag{4}$$

where k_0 is the wavenumber of the radiation. This scattering is polarization dependent and has a polarization in the direction of the dipole moment $\mathbf{P}$.[21] For a single resonance such that $k=1$, the scattering cross section in terms of the phase shift of the resonance is

$$C_{\text{sca}} = \frac{{k_0}^4}{6\pi}\left|\frac{a_j^1(\omega_R)\mathbf{p}_j^1}{E_0}\right|^2 \cos^2\phi. \tag{5}$$

For small phase shifts, the scattering cross section is almost constant and varies as $1-\phi^2$. It is the spectrum generated by this cross section as the frequency of the incident light is varied that is used in single nanoparticle systems to detect perturbations to the local electric permittivity. The limitation with this method is the large scattering in the absence of a phase shift and the small relative change ${C_{\text{sca}}}^{-1}(dC_{\text{sca}}/d\phi) \sim -2\phi$ for small phase shifts. This large offset is removed in the Wheatstone bridge circuit.

The proximity of one nanoparticle to another modifies the resonances because of the mutual interaction between the induced electric fields and the charges associated with the

surface plasmons. In circuit theory this would be interpreted as a capacitive coupling. The interaction between the nanoparticles can be modeled using coefficients C_{ij}^{lk} that describe the effect of the electric field from the kth mode of particle j on the surface dipole distribution of the lth mode of particle i. For simplicity we assume that the frequency of the incident light is close to the dominant resonance of each nanoparticle so that we can ignore all but one of the eigenmodes, which we label with the superscript $k=1$. Let $\tilde{a}_j^k$ be the amplitudes modified by the coupling between nanoparticles. Then using the theory of Davis *et al.*,[16] the modified amplitudes for a three particle system are given in a matrix form

$$\begin{bmatrix} \tilde{a}_1^1 \\ \tilde{a}_2^1 \\ \tilde{a}_3^1 \end{bmatrix} = \begin{bmatrix} a_1^1 \\ a_2^1 \\ a_3^1 \end{bmatrix} + \begin{bmatrix} 1 & -C_{12}^{11} & -C_{13}^{11} \\ -C_{21}^{11} & 1 & -C_{23}^{11} \\ -C_{31}^{11} & -C_{32}^{11} & 1 \end{bmatrix}^{-1} \begin{bmatrix} 0 & C_{12}^{11} & C_{13}^{11} \\ C_{21}^{11} & 0 & C_{23}^{11} \\ C_{31}^{11} & C_{32}^{11} & 0 \end{bmatrix} \times \begin{bmatrix} a_1^1 \\ a_2^1 \\ a_3^1 \end{bmatrix}. \tag{6}$$

Taking the nanoparticle system of Fig. 1(a) and assuming that the direct coupling between the sense and reference arms of the bridge (nanoparticles 1 and 2) is small, but there is strong coupling to the bridging antenna (nanoparticle 3), we have $C_{12}^{11}=C_{21}^{11}\approx 0$. Furthermore, if the incident light is polarized in the y direction, $\mathbf{E}_0=E_0\hat{\mathbf{y}}$, then the excitation amplitude of the antenna nanoparticle is zero $a_3^1=0$. This is because nanoparticle 3 is oriented with its long axis in the x direction so that its fundamental resonance has a dipole moment $\mathbf{p}_3^1=p_3^1\hat{\mathbf{x}}$ [see Eq. (2)]. However, a surface plasmon can be induced in this nanoparticle by the coupling of the electric fields from the reference and the sense nanoparticles. Applying these conditions to Eq. (6) we arrive at

$$\begin{bmatrix} \tilde{a}_1^1 \\ \tilde{a}_2^1 \\ \tilde{a}_3^1 \end{bmatrix} = \frac{1}{\Delta} \begin{bmatrix} 1-C_{23}^{11}C_{32}^{11} & C_{13}^{11}C_{32}^{11} & C_{13}^{11} \\ C_{23}^{11}C_{31}^{11} & 1-C_{13}^{11}C_{31}^{11} & C_{23}^{11} \\ C_{31}^{11} & C_{32}^{11} & 1 \end{bmatrix} \begin{bmatrix} a_1^1 \\ a_2^1 \\ 0 \end{bmatrix}, \tag{7}$$

where the determinant is

$$\Delta = 1 - C_{23}^{11}C_{32}^{11} - C_{13}^{11}C_{31}^{11}. \tag{8}$$

Our design of the plasmonic circuit of Fig. 1(a) has a high degree of symmetry that greatly simplifies the analysis. Since the sense and reference nanoparticles are identical, but are arranged symmetrically at either end of the antenna nanoparticle, it is straightforward to show that $C_{31}^{11}=-C_{32}^{11}$. This is due to the fact that the fundamental resonance for these nanoparticles is a dipole mode that has opposite charges at each end. Then the excitation amplitude for nanoparticle 3 is given by

$$\tilde{a}_3^1 = \frac{C_{31}^{11}(a_1^1 - a_2^1)}{1 - C_{23}^{11}C_{32}^{11} - C_{13}^{11}C_{31}^{11}} = C_{31}^{11}(\tilde{a}_1^1 - \tilde{a}_2^1). \tag{9}$$

This shows that the amplitude of the dipole moment induced in the antenna is proportional to the difference between the dipole moments of the sense and reference nanoparticles. The balanced condition for the Wheatstone bridge is when $a_2^1=a_1^1$ or $\tilde{a}_2^1=\tilde{a}_1^1$ for which the antenna has no induced dipole moment, $\mathbf{P}_3=0$, and therefore does not radiate light. Under this condition, the nanoparticle system of Fig. 1(a) would scatter light with the same polarization as the incident beam.

If there is a perturbation in the surrounding dielectric, such as the binding of molecules to the sense nanoparticle, then the response of the system due to the shift in the resonance of the nanoparticle is found using Eq. (3). Assuming that nanoparticles 1 and 2 have the same amplitude at resonance $\tilde{a}_1^1(\omega_R)=\tilde{a}_2^1(\omega_R)\equiv\tilde{a}(\omega_R)$ then

$$\tilde{a}_3^1 = C_{31}^{11}\tilde{a}(\omega_R)(\cos\,\phi\,\exp(i\phi) - 1), \tag{10}$$

and the scattering cross section for the antenna nanoparticle 3 is given by

$$C_{\mathrm{sca}} = \frac{{k_0}^4}{6\pi}\left|\frac{C_{31}^{11}\tilde{a}(\omega_R)\mathbf{p}_3^1}{E_0}\right|^2 \sin^2\,\phi. \tag{11}$$

The light emitted from the antenna is polarized in the direction of $\mathbf{p}_3^1=p_3^1\hat{\mathbf{x}}$, which is perpendicular to the incident polarization. This provides a practical means by which the imbalance in the plasmonic circuit can be detected. A polarizer can be used to filter out the incident light scattered from the sense and reference arms and only the scattered light from the antenna nanoparticle will be detected. Unlike the single nanoparticle, the system of nanoparticles in an ac Wheatstone bridge configuration responds to small phase shifts or small perturbations in the surrounding dielectric with light scattering that varies rapidly with phase, in proportion to $|C_{31}^{11}|^2\phi^2$. In effect we have nulled the constant term in Eq. (5), which has a different polarization, and we have a scale factor C_{31}^{11} for adjusting the sensitivity of the circuit. The relative change for small phase shifts ${C_{\mathrm{sca}}}^{-1}(dC_{\mathrm{sca}}/d\phi) \sim 2/\phi$ is now very large.

There are a number of factors that can result in an imbalance in the plasmonic circuit, such as (i) a change in the coupling efficiency of the polarized light to one of the nanoparticles; (ii) a variation in shape of a nanoparticle, which leads to a change in the eigenmode (and eigenvalue); or by (iii) a change in the background electric permittivity. In terms of the equivalent circuit model of Fig. 1(b), these correspond to changes in the capacitance C_E, a change in the impedance Z, or a change in the capacitance associated with Z [see Fig. 1(c)]. For sensing applications, it is the binding of molecules to one of the nanoparticles (such as the sense nanoparticle 1) that leads to a change in the local background permittivity. In Sec. III we use a numerical model to simulate the binding of molecules to nanoparticle 1 and to calculate the response of the plasmonic Wheatstone bridge.

III. SIMULATION

In this section we provide a numerical example of the operation of the plasmonic circuit using a simple dipole model for the interaction of molecules with the surface of nanoparticle 1 and estimate and compare its ability to sense molecules. We treat each molecule as a sphere of radius r_{mol}, electric permittivity $\varepsilon_{\mathrm{mol}}$, and polarizability $4\pi r_{\mathrm{mol}}^3(\varepsilon_{\mathrm{mol}}$

TABLE I. The parameters for the molecule dipole model and the dimensions of the plasmonic circuit components relative to the length of the nanoparticles.

	Width x	Length y	Thickness z
Nanoparticles	0.43	1.00	0.29
Dipole patch	0.29	0.18	···
	Center-center distance		
Nanoparticles 1 and 2	2.57		
	Radius	Permittivity	
Dipole	$r_{mol}=0.0071$	$\varepsilon_{mol}=2.13$	

$-\varepsilon_b)/(\varepsilon_{mol}+2\varepsilon_b)$.[21] Later we will consider the detection of biological molecules, such as proteins, which bind near the surface of the plasmonic particle. For the dipole model we assume a permittivity $\varepsilon_{mol}\sim 2.13$, which is a value found in biological materials.[22] The effect of the electrical polarization of the molecules is averaged over the patch at one end of the sense arm (nanoparticle 1) shown in Fig. 1(a).

As discussed in Sec. II, the sensitivity of the plasmonic circuit depends on the coupling coefficient C_{31}^{11}. This coefficient includes a factor related to the resonance of the bridging antenna nanoparticle.[16] The coefficient is large when the geometry of the antenna is designed to resonate at the frequency of the incident light. Furthermore, the scattering cross section depends on the coefficient $\tilde{a}(\omega_R)$, which can also be large when the resonances of the sense and reference nanoparticles coincide with the frequency of the incident light. For convenience, we choose all nanoparticles to have the same dimensions. Other than adjusting the separation between the nanoparticles to obtain good resonances, we have made no attempt to optimize the circuit.

The geometry of the nanoparticles used in our model is given in Table I. The nanoparticles are made from gold, with a complex, frequency-dependent permittivity,[23] are placed on a glass substrate ($\varepsilon_s=2.31$), and immersed in water ($\varepsilon_b=1.77$). With these parameters we determine the set of eigenmodes for the nanoparticles[17] and then use the coupling theory[16] to calculate the amplitudes $\tilde{a}_j^1$, the induced dipole moments $\mathbf{P}_j$, and the radiated light, expressed in terms of scattering cross sections C_{sca}^x and C_{sca}^y for each polarization direction x and y. The incident light is polarized in the y direction. Note that, within the approximations of the electrostatic theory, the excitation amplitudes are scale independent so that only the aspect ratios of the nanostructures are important. However, the calculations of the scattering cross sections require a scale to give them the dimensions of area. To begin with we keep the simulations scale independent and normalize the scattering cross sections to give relative values, as discussed below.

The spectrum of x-polarized light scattered from the plasmonic bridge circuit is shown in Fig. 2 for different numbers N of dipoles distributed over the patch on the sense arm (nanoparticle 1). The spectrum is expressed in terms of the scattering cross section normalized to the maximum of C_{sca}^y with $N=0$. There is also a slight shift in the wavelength of the maximum, which is related to the effective change in the

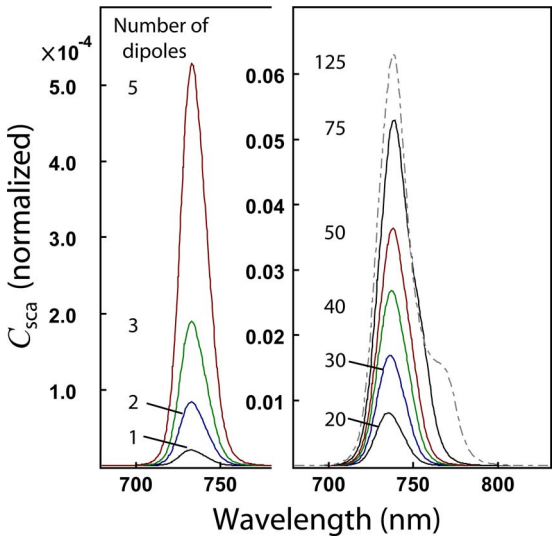

FIG. 2. (Color online) The spectrum of x-polarized light radiated from the antenna nanoparticle 3 for different numbers of dipoles distributed over the patch on the sense nanoparticle 1.

electric permittivity. This shift is also seen in C_{sca}^y and it is the quantity that would be measured in single nanoparticle systems, as in Eq. (5), to determine the change in the local permittivity. For the plasmonic circuit, there are a number of resonating elements that shift out of phase with one another as molecules bind to nanoparticle 1, which eventually cause the resonances to move apart. This is the origin of the asymmetry in C_{sca}^x for $N=125$. The wavelength shift is almost indiscernible until the resonances split at large N. The key feature from Fig. 2 is the absence of an optical signal when the system is balanced (no dipoles, $N=0$) and a rapid increase in this signal as more dipoles attach to the surface of nanoparticle 1. The signal varies from about 0.01% of C_{sca}^y for $N=1$ to 6% when $N=125$. The ultimate sensitivity of the circuit depends on our ability to detect this scattering. For comparison, the normalized scattering cross sections for x- and y-polarized light as functions of the number of dipoles are shown in Fig. 3. This also includes the wavelength shift of the center peak.

The physical origin of the signal from the antenna nanoparticle 3 is the change in the relative phase of the resonances in the sense and reference nanoparticles 1 and 2, as

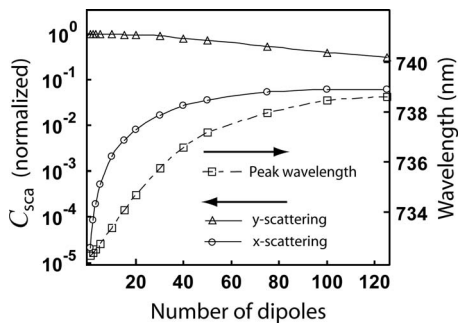

FIG. 3. The maxima of the normalized scattering cross sections for light scattering with polarizations x (circles) and y (triangles) as functions of the number of dipoles distributed over the patch on the sense nanoparticle 1. Also in the figure is the wavelength of the peak in the scattering cross section (squares).

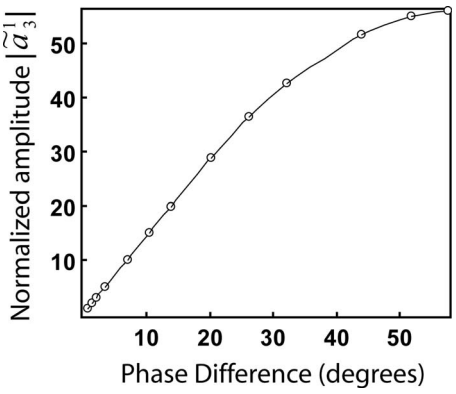

FIG. 4. The magnitude of the amplitude $|\tilde{a}_3^1|$ vs the phase difference between the two arms (nanoparticles 1 and 2) of the circuit, demonstrating the linear dependence on phase. The amplitude is normalized to its value for a single dipole.

described by Eqs. (10) and (11). To model the sensitivity of the circuit to the phase shifts, we use our numerical simulation to calculate the magnitude of the amplitude $|\tilde{a}_3^1|$ as a function of the phase difference between the oscillations in the arms of the bridge. The results are shown in Fig. 4. This shows that the amplitude varies linearly with phase ϕ up to about 30°. This is consistent with the magnitude of Eq. (10) where $|\tilde{a}_3^1| \propto \sin \phi$. The scattering cross section, which gives an indication of the measured signal, depends on $|\tilde{a}_3^1|^2$ so that the signal intensity is a direct measure of the phase difference between the oscillations in the two nanoparticles.

In this section we have provided results of a simulation of the binding of molecules to the sense arm of the plasmonic Wheatstone bridge and shown that the scattering cross section for light polarized perpendicular to the incident light increases rapidly with the number of dipoles. Furthermore the simulations show that the optical output from the circuit gives a measure of the phase shift between the localized SPRs in the two arms of the bridge, which is consistent with our analysis in Sec. II. In the section below we consider the detection of single large molecules using the circuit and some practical considerations required for its implementation.

IV. SINGLE-MOLECULE DETECTION

One aspect of the electrostatic theory is that it is scale independent,[17] provided that the nanostructures are much smaller than the wavelength of the incident light. This is also true for the dipole model we used to determine the effect of molecules adhering to the surface of the sense arm, nanoparticle 1. However, we would like to determine if the scattering from the plasmonic bridge circuit is measureable and to calculate this we need to set a scale. If the length of each nanoparticle is chosen as 100 nm, then keeping the same aspect ratios from Table I, the widths are 43 nm, thickness is 29 nm, and the molecule dipole radius becomes 0.71 nm. The typical radius of an organic molecule, such as a protein, is about 2 nm.[24] Because of the volume dependence of the electric polarization, we would need $N=22$ of these dipoles to be equivalent to one protein of 2 nm radius. In terms of the scattering cross section, from Fig. 2, we find that the signal from the bridge circuit due to 22 dipoles is equivalent to about 1% of the light scattering with a polarization parallel to the incident light. Light scattering from a single nanoparticle can be observed easily using total internal reflection[25] or dark-field illumination.[26] Furthermore, polarizers are readily available that have extinction ratios exceeding 10 000:1 so we would expect no difficulty in observing the output of the plasmonic circuit at 1% of the intensity measured in single nanoparticle experiments.

The usual measurements of light scattering from single nanoparticles are spectrally resolved. For example, in the experiments on the binding of the protein streptavidin to 40 nm diameter gold nanoparticles, the surface plasmon peak at 544.4 nm shifts by about 1.2 nm.[9] From an experimental viewpoint we do not need to spectrally resolve the optical signal from the plasmonic circuit, since it is the amplitude of the light scattering that conveys the information. This allows us to use a detector that integrates over the spectrum. This greatly improves the performance of this system relative to those that rely on measuring the spectral shift. From Fig. 3, a spectral measurement would need to resolve a spectral shift of about 3 nm to detect the presence of a protein molecule (that is a shift from $N=0$ to $N=20$). If we integrate over the spectral peak for $N=20$, the integrated scattering cross section increases from about 0.8% to 16% of the maximum (nonintegrated) scattering, which is a significant increase in the measured signal. This suggests that the plasmonic Wheatstone bridge circuit has the potential to detect the adsorption of a single protein molecule on its surface. The key to this is the separation of the incident light from the output light using a suitable polarizer and the practical success depends on there being low levels of random scattering, as might arise from contamination, that change the polarization.

There are some practical considerations that need to be addressed to apply this circuit to detecting protein molecules. First, the reference arm and the output antenna need to be isolated from the sample. That is, we require the molecules to adsorb only on the sense arm of the plasmonic circuit. This condition can be met by coating the entire circuit with an isolating material and using lithographic methods to create an opening on the sense arm, such as the patch in Fig. 1(a), that can be exposed to the sample solution. Ideally, the isolating material is chosen to have a refractive index matching that of the sample solution, or at least close to it. For example, MgF_2 is a standard optical material with a refractive index of 1.37, which is similar to water with a refractive index of 1.33. To achieve selectivity, the opening on the sense arm is coated with an antibody layer that will bind predominantly to the target molecule. Such coatings are used routinely in SPR biosensors, such as that described by Feltis *et al.*,[27] and are attached using thiol chemistry that binds preferentially to the gold surfaces.

The second consideration is balancing the circuit. This is more problematic, particularly when coatings are used that are different for the sense and reference arms of the circuit. As discussed in Sec. II, there are a number of factors that can imbalance the plasmonic circuit, which therefore can be used to balance it. This may include changing the electric permittivity of the sample solution, which predominantly affects

the sample arm through the opening; changing the geometry of one of the arms to shift the resonances closer; and placing another nanostructure nearby one of the arms so that the additional coupling shifts the resonance. In principle the circuit can be fabricated with each arm having an appropriate geometry such that the circuit becomes balanced when the various coatings are applied and the circuit is placed in the sample solution. However, there are always imperfections in the lithographic process that cause variations in the design geometry, making the balancing more difficult. In this regard it is desirable to balance the circuit *in situ* after fabrication. There are a variety of ways in which this might be achieved and we present two examples. If the sample solution and the protective coating have refractive indices that are close to one another, it is possible to modify the refractive index of the sample solution with additives, such as sucrose,[27] until balance is obtained. Alternatively the geometry of the sense arm could be modified by adding or removing small amounts of material using processes such as electrodeposition and electroetching. If the circuit is fabricated on a transparent conducting layer, for example, indium-doped tin oxide, an electrical connection to the plasmonic elements can be established. Small amounts of metal from the exposed region on the sense arm can be applied or removed by placing the circuit in a suitable electrolyte and applying an electrical potential. In this method, the rest of the circuit is protected by the nonconducting MgF_2 layer. During the deposition or etching process, the output signal from the bridge can be monitored, either to achieve balance or to achieve the desired offset so that balance is obtained when the device is coated with the antibody and placed in the sample solution (which may be different from the electrodeposition/etching solution).

If the circuit is not perfectly balanced, it still has an advantage over other methods in that it produces a change in the intensity of the x-polarized component of the scattered light with adsorption of molecules. The degree of balance required for the detection of single protein molecules depends on the experimental arrangements and our ability to measure small intensity changes. For large imbalances the sensitivity of the circuit is greatly reduced since the relative phase shift between the arms is smaller. For example, a large imbalance means that the phase difference between the sense and reference arms will be close to 90°. From Eq. (11) we see that the scattering cross section will vary as $1-\Delta\phi^2$ with small changes $\Delta\phi$ in the phase about $\phi=\pi/2$. This is equivalent to the single nanoparticle sensor as modeled by Eq. (5). In this regard it is important to achieve some degree of balance of the circuit to take full advantage of it.

V. CONCLUSIONS

In conclusion, we have presented the first plasmonic circuit equivalent of the ac Wheatstone bridge and shown that an optical signal is produced that is related to the imbalance between the two arms of the circuit. Furthermore, the analysis shows that the amplitude of the induced dipole moment in the bridging antenna nanoparticle is proportional to the phase difference between the signals in the sense and reference arms. This means that the optical signal gives a direct measure of the phase difference. The sensitivity of the circuit was discussed and it was shown that it has the potential to detect the presence of a single large molecule, such as a protein, adsorbing on its surface. This circuit potentially provides higher sensitivity and easier detection of perturbations to the surrounding media compared with the standard single nanoparticle, plasmon sensor.

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